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Copper-Catalyzed Intramolecular Oxidative C–H Functionalization and C–N Formation of 2-Aminobenzophenones: Unusual Pseudo-1,2-Shift of the Substituent on the Aryl Ring

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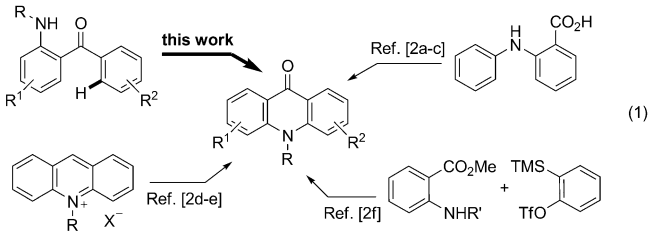
Highly-substituted acridones are versatile building blocks for many naturally occurring products and have attracted much attention due to their unique biological activities.[1] They are important antileishmanial, antifungal, antitumor, and DNA-intercalating anticancer drugs.[1d] The classical routes to the synthesis of acridones rely on the acid-induced ring-closure of *N*-phenyl anthranilic acids,[2a–c] oxidation of the corresponding acridinium salts by molecular oxygen under basic conditions,[2d–e] coupling of 2-aminobenzoate with arynes in the presence of CsF,[2f] in addition to a few other methods.

In recent years, the transition-metal-catalyzed directed transformation of an inactivated C–H bond into various new functional groups has emerged as a powerful method in organic synthesis.[3] In particular, the C–C, C–N, and C–O bond formation from C–H activation catalyzed by ruthenium, rhodium, and palladium complexes has been extensively studied.[4] Compared with those reported methods, the use of cost effective and low toxic copper complexes as catalysts for these transformations is much less explored.[5] In 2008, an intramolecular Cu^{II}-catalyzed C–N bond formation of amidines to form benzimidazoles using O_2 as the oxidant was reported by Buchwald et al.[6] At about the same time, Nagasawa and Ueda developed a copper-catalyzed intramolecular oxidative C–O bond formation of benzanilides leading to functionalized benzoxazoles.[7] Recently, Zhu and co-workers reported the synthesis of pyrido[1,2-*a*]benzimidazoles from *N*-aryl-2-aminopyridines through direct intramolecular aromatic C–H amination co-catalyzed by Cu^{II} and Fe^{III}.[8] Chang et al. reported a copper-catalyzed synthesis of functionalized carbazoles through the directed intramolecular oxidative C–N bond-forming reaction of *N*-substituted 2-amidobiphenyls.[9] To date, most oxidative C–N bond formations lead to five-membered heterocyclic compounds including the synthesis of carbazoles, benzimidazoles, indazoles,[4j] indolines,[10] *N*-methoxylactams,[11] and imidazobenzimidazole.[12] For instance, a Pd^{II}-catalyzed intramolecular C–H amination reaction to synthesize indolines and methoxylactams was reported by Yu et al.[10a,11] Glorius and co-workers demonstrated a palladium-catalyzed synthesis of indolines from anilides through a C–H bond activation reaction.[10b] A copper-catalyzed C–H amination leading to imidazobenzimidazoles[12] and 4-aryl-2-quinolones[14] was also described.

Our continued interest in the metal-catalyzed C–H bond activation[13a–g] and synthesis of heterocyclic compounds reactions[13h–k] prompted us to explore the oxidative coupling reaction of 2-aminobenzophenones. Herein we wish to report a copper(I)-catalyzed intramolecular oxidative C–H bond functionalization and C–N coupling of 2-aminobenzophenones to give 6-membered-ring acridone products.[15]



(1)

Treatment of 2-aminobenzophenone **1a** in the presence of CuI (1.0 mol%) and 2,2′-bipyridine (bpy, 1.0 mol%) in dimethylacetamide (DMAc) at 140°C for 12 h under an oxygen atmosphere gave product **2a** isolated in 97% yield (Table 1, entry 1). The structure of **2a** was confirmed by its ^1H, ^{13}C NMR spectra and mass data.

This copper-catalyzed oxidative coupling reaction depends greatly on the reaction conditions. To understand the nature of this reaction and to find the optimized reaction conditions, the activity of various copper complexes and the effect of nitrogen ligand and solvent on the product yield were examined (see the Supporting Information for detailed studies). CuI (1.0 mol%) in bpy (1.0 mol%) is the most effective combination, forming the oxidative C–N coupling product **2a** isolated in 97% yield (Table 1, entry 1). Other copper catalysts (1.0 mol%) such as CuCl, $CuCl_2$, CuBr, CuO, Cu_2O, $Cu(acac)_2$, $Cu(OTf)_2$ and $Cu(OAc)_2$ in the presence of bpy (1.0 mol%) were less effective giving **2a** in 16, trace, 20, 12, 48, trace, trace and 50% yields, respectively.

The presence of a nitrogen ligand was crucial to the reaction. Among the nitrogen ligands that we examined, 2,2′-bi-

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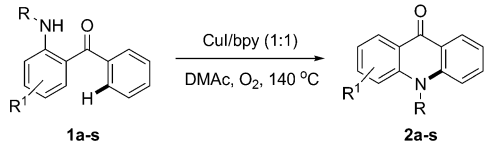
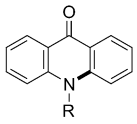
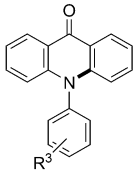
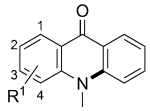
Table 1. Results of the copper-catalyzed oxidative C–N coupling of 2-aminobenzophenones.[a]



1a-s 2a-s

Entry	Product		2	Cat. [mol%]	t [h]	Yield [%][b]
1		R=Me	2a	1	12	97
2		R=*i*Pr	2b	10	36	59
3		R=*n*-Pr	2c	10	24	57
4		R=H	2d	10	24	35
5		R^3=H	2e	0.5	15	98
6		R^3=3-Me	2f	0.5	12	93
7		R^3=4-OMe	2g	0.5	22	89
8		R^3=2-OMe	2h	1	24	92
9		R^3=4-F	2i	0.5	18	95
10		R^3=4-Br	2j	1	24	93
11		R^3=4-CN	2k	2	24	84[c]
12		R^3=4-CO_2Me	2l	2	18	81[c]
13		R^3=4-CF_3	2m	5	24	92[c]
14		R^1=1-F	2n	10	12	60
15		R^1=2,3-OMe	2o	1	12	98
16		R^1=3-Me	2p	1	12	96
17		R^1=2-Br	2q	1	24	96[c]
18		R^1=3-Cl	2r	1	18	95
19		R^1=2-Cl	2s	1	18	90

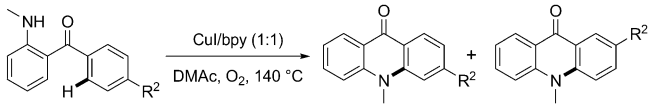
[a] The reactions were carried out by using 2-aminobenzophenone **1** (0.5 mmol), CuI (1.0 mol%), bpy (1.0 mol%), and DMAc (1.0–5.0 mL) at 140°C under O_2. [b] The yield is of the isolated products. [c] The reaction was carried out at 150°C.

pyridine gave the best result affording **2a** in 97% yield. Other nitrogen ligands including pyridine, 3,4,7,8-tetramethyl-1,10-phenanthroline, 1,10-phenanthroline, 4,4′-dimethyl-2,2′-bipyridine, 3,3′-biisoquinoline, *trans*-1,2-diaminocyclohexane, and TMEDA are less effective, giving **2a** in 41, 23, 40, 58, 75, 71, and 66% yield, respectively. The effect of solvent to the catalytic reaction was also studied. Dimethylacetamide (DMAc) was found to be the ideal solvent affording **2a** in 97% yield. Other solvents such as DMF, DMSO, *ortho*-dichlorobenzene (*o*-DCB) and *o*-xylene were less effective for the catalytic reaction giving **2a** in 39, 6, 71, and 13% yield, respectively.

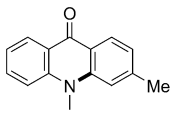
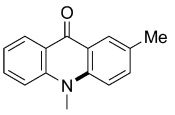
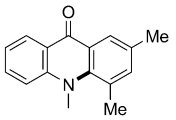
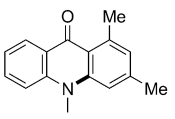
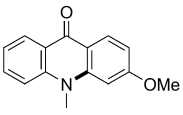
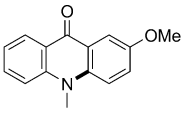
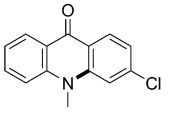
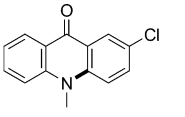
Under the standard reaction conditions, several *N*-alkyl substituted aminobenzophenones were examined (Table 1). Thus, *N*-isopropyl, **1b**; *N*-propyl, **1c** gave the corresponding acridones **2b–c** in moderate yields (Table 1, entries 2 and 3). Interestingly, the unsubstituted 2-aminobenzophenone **1d** also provided acridone **2d** in 35% yield (Table 1, entry 4). The C–H activation and C–N bond-formation reaction also works well with *N*-aryl substituted aminobenzophenones. Accordingly, *N*-phenylaminobenzophenone **1e** gave acridone **2e** in 98% yield (Table 1, entry 5). Similarly, aminobenzophenones **1f–h** with electron-donating groups, 3-methyl, 2-methoxy and 4-methoxy on the *N*-phenyl ring afforded the corresponding C–N bond-formation product **2f–h** in excellent yields (Table 1, entries 6–8). In a similar manner, electron-withdrawing substituents on the *N*-aryl ring of the aminobenzophenone were well tolerated (Table 1, entries 9–13). It is noteworthy that the structure of compound **2i** was further confirmed by single-crystal X-ray diffraction.[20] The effect of the substituents on the phenyl ring (R^1) of aminobenzophenones was also investigated. Thus, aminobenzophenones **1n–s** underwent intramolecular C–N bond formation effectively to give the corresponding acridones **2n–s** in good to excellent yields (Table 1, entries 14–19). It is noteworthy that other aminobenzophenones with substituents such as Boc, Ac, Bn, and Ts on the amino group did not undergo the expected cyclization to give the corresponding acridones.

The CuI/bpy-catalyzed oxidative cyclization reaction of aminobenzophenones **1** having different substituents (R^2) on the phenyl ring was also examined. To our surprise, treatment of **1t** having a methyl substitution at the *para* position under the standard conditions gave two regioisomers **2p** and **2p′** in a 5:2 ratio in a combined yield of 98% (Table 2, entry 1). The main product **2p** exhibits the expected acridone structure with the methyl substituent *para* to the keto group, whereas the minor acridone product **2p′** has the methyl substituent *meta* to the keto and *para* to the amino group. Both products

Table 2. Products of copper-catalyzed oxidative C–N coupling of 2-aminophenyl aryl ketones.[a]



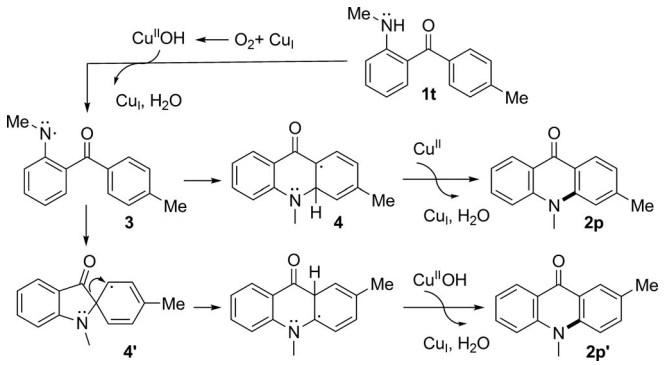
1 2 (major) 2′ (minor)

Entry	1	Products (major)		(minor)		t [h]	Yield [%][b]
1	1t		2p		2p′	12	98 (5:2)
2	1u		2u		2u′	24	94 (3:2)
3	1v		2v		2v′	18	96 (6:1)
4	1w		2r		2s	24	96 (1:1)[c]

[a] The reactions were carried out using 2-aminobenzophenone **1** (0.5 mmol), CuI (1.0 mol%), bpy (1.0 mol%), and DMAc (1.0–5.0 mL) at 140°C under O_2. [b] Yield is of the isolated product. [c] The reaction was carried out with CuI (2.0 mol%) and bpy (2.0 mol%).

2p and **2p′** can be separated by column chromatography and were well characterized. Similarly, other 2-aminobenzophenones **1v** and **1w** with *para*-methoxy and chloro substituent(s) on the phenyl ring, respectively, also gave the corresponding acridones having two regioisomers (Table 2, entries 3–4). The formation of two regioisomeric products from 2-aminobenzophenone derivative with substituent(s) on the phenyl ring appears general. Treatment of 2-aminophenyl *m*-dimethylphenyl ketone **1u** under the standard reaction conditions also afforded two isomeric product **2u** and **2u′** in a 3:2 ratio in an excellent combined yield. For product **2u**, the two methyl groups are all *meta* to the keto group, whereas for isomer **2u′**, the two methyl substituents are *meta* to the amino group. Compared with the structure of the major product, the minor isomer in each reaction appears to have a structure with the substituents on the phenyl ring undergoing 1,2-shift toward the keto group as shown in Table 2.

The mechanism of the present catalytic reaction is not yet clear. There are several types of mechanisms proposed to account for the copper-catalyzed organic reactions.[5–9,16] Based on the observed rearrangement product **2′**, which strongly suggests an *ipso* to *ortho* migration of the keto group on substrate **1**, we propose a hydrogen abstraction (or one-electron oxidation followed by proton dissociation) and radical cyclization pathway as shown in Scheme 1 for the



Scheme 1. Proposed mechanistic pathway for the formation of acridone.

present catalysis.[17] The catalytic reaction is likely initiated by the interaction of Cu^{I} with O_2 to generate a Cu^{II} hydroxide. Abstraction of a hydrogen atom from the amino group of substrate **1t** forms an *N*-centered radical **3**. Addition of the amino radical to the neighboring aryl group gives two possible intermediates: a 6-membered radical **4** and a 5-membered radical **4′**. Hydrogen abstraction of **4** by Cu^{II} hydroxide leads to the final product acridone **2p**. For the radical intermediate **4′**, migration of the keto group to the *ortho* carbon followed by hydrogen abstraction affords regioisomer **2p′**. The formation of **2p′** can be considered as a pseudo-1,2-migration of the substituent (methyl) on the arene ring.

It is interesting to note that we were able to isolate two possible copper complexes that are likely the catalytic intermediates (Figure 1). From the solution of CuI and bpy (1:1), we isolated the Cu^{I} dimer, $[Cu(bpy)I]_2$, of which the structure was determined by X-ray diffraction as shown in structure **A**.[20] The reaction of **A** with O_2 (1 atm) in DMSO at room temperature gave a tetrameric Cu^{II} species **B** $\{[(bpy)Cu^{II}OH]_2(DMSO)\}_2^{4+}(I^-)_4$. Single crystals of **B** were obtained from the solution and the structure was determined by X-ray diffraction.[20] **B** can also be isolated from **A** in the presence of O_2 and substrate **1**. It is noteworthy that **B** is 4^+ cationic species with I^- as the anion. Complex **B** reacted with **1a** (1:1 molar ratio) in DMAc under a nitrogen atmosphere to give product **2a** (64% yield) and dimer **A** as precipitate. Furthermore, the use of **B** (1.25 mol%) as the catalyst for cyclization of **1a** in DMAc under O_2 atmosphere at 140°C gave **2a** in 99% yield. These results indicate that **A** and **B** are likely intermediates for the present copper-catalyzed oxidative cyclization.

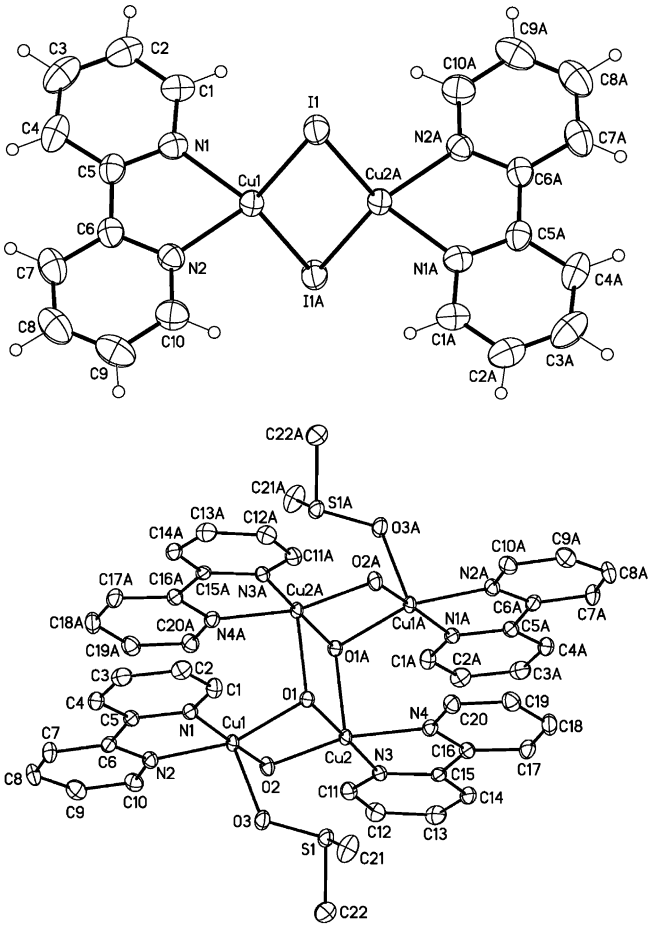
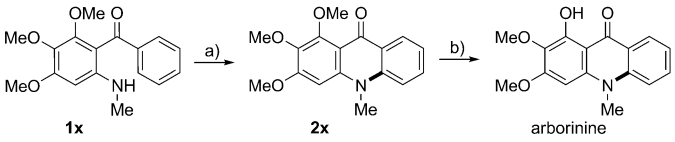


Figure 1. ORTEP representation of $[Cu(bpy)I]_2$ (**A**) and $\{[(bpy)Cu^{II}OH]_2(DMSO)\}_2^{4+}(I^-)_4$ (**B**). Thermal ellipsoids are set at 50% probability.

To find evidence to support that the mechanism involves a radical reaction, we examined the oxidative cyclization of **1a** under the standard reaction conditions except in the presence of BHT (2,6-di-*tert*-butyl-4-methylphenol), which is a known inhibitor of radical reactions. Thus, if BHT (1 mol%) was added to the reaction solution, compound **2a**

was obtained in 55% (yield obtained from NMR spectroscopy); whereas if 5 mol% of BHT was used, only a trace of **2a** was detected. These results support that the catalytic reaction goes through a radical mechanism.

The significance of this copper-catalyzed intramolecular C–N bond-formation reaction is demonstrated by its application to the total synthesis of an acridone natural product arborinine. The synthetic Scheme by using this methodology as the key step is shown in Scheme 2. Thus, treatment of



Scheme 2. Total synthesis of arborinine. a) CuI (1.0 mol%), 2,2′-bipyridine (1.0 mol%) and DMAc, 160°C, 12 h, 96%; b) conc. HCl (20.0 equiv), MeOH, heat at reflux, 12 h, 84%.

aminobenzophenone **1x** in the presence of CuI and bpy in DMAc at 160°C for 12 h provided **2x** in 96% yield. After a successful acid-catalyzed selective demethylation reaction of **2x**, we obtained arborinine in 84% yield. The overall yield of arborinine from **5** was 43%, which is much higher than those reported earlier.[18] It is interesting to note that arborinine has been shown to exhibit several biological effects.[19]

Interestingly, the present catalytic reaction also proceeded smoothly on a 10.0 mmol scale of substrate **1a** under the standard reaction conditions. Product **2a** was readily isolated in 85% yield.

In conclusion, we have successfully developed a CuI/bpy-catalyzed synthesis of acridone derivatives through C–H functionalization and C–N bond formation of 2-aminobenzophenone in one pot. The protocol generally requires very low catalyst loading (1.0 mol%) and is successfully applied to the total synthesis of arborinine with excellent yield. Furthermore, the present catalytic reaction involves an unusual pseudo-1,2-migration of the substituent on the arene ring leading to the formation of two regioisomers.

Experimental Section

General procedure for the copper-catalyzed synthesis of acridone: A sealed tube containing CuI (1.0 mol%) and 2,2′-bipyridine (1.0 mol%), was evacuated and purged with oxygen gas three times. Then, DMAc (1.0–5.0 mL), 2-aminobenzophenone **1a** (0.50 mmol), were sequentially added to the system through a syringe under an oxygen atmosphere and the reaction mixture was allowed to stir at 140°C for 12 h. When the reaction was completed, the mixture was cooled and diluted with CH_2Cl_2 (10 mL). The mixture was filtered through a Celite and silica gel pads and was washed with CH_2Cl_2/MeOH (50 mL). The combined filtrate was concentrated and the residue was purified by a silica gel column by using hexane/EtOAc as eluent to give pure **2a** in 97%.

Acknowledgements

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Keywords: acridones · aminobenzophenone · bipyridine · copper · oxidation · total synthesis

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[20] CCDC-911172 (**2i**), CCDC-911171 (**A**), and CCDC-911170 ($\{[(bpy)Cu^{II}OH]_2(DMSO)\}_2^{4+}(I^-)_4$, **B**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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